CC=JP DATE=19790919 KIND=Kokai PN=54120675

METHOD FOR MANUFACTURING AN UNSATURATED POLYESTER RESIN PANEL

[Fuhowa Poriesuteru Jushi Ban no Sei Ho]

Akitsugu Miwa, Yoshihiro Kitsuda, and Takeshi Murakami

| PUBLICATION COUNTRY           | (10):  | JP  |
|-------------------------------|--------|---|
| DOCUMENT NUMBER               | (11):  | 54120675  |
| DOCUMENT KIND                 | (12):  | Kokai   |
| PUBLICATION DATE              | (43):  | 19790919  |
| APPLICATION NUMBER            | (21):  | 53-29065  |
| APPLICATION DATE              | (22):  | 19780313  |
| INTERNATIONAL CLASSIFICATION  | (51):  | B 29 D 3/02//<br>B 29 C 27/12<br>B 32 B 15/08<br>B 32 B 27/36<br>B 32 B 27/38<br>B 32 B 31/12 |
| PRIORITY COUNTRY              | (33):  | N/A   |
| PRIORITY NUMBER               | (31):  | N/A   |
| PRIORITY DATE                 | (32):  | N/A   |
| INVENTOR(S)                   | (72):  | Akitsugu Miwa,<br>Yoshihiro Kitsuda, and<br>Takeshi Murakami                                  |
| APPLICANT(S)                  | (71):  | Matsushita Denko Co.,<br>Ltd.   |
| DESIGNATED CONTRACTING STATES | (81):  | N/A   |
| TITLE                         | (54):  | METHOD FOR<br>MANUFACTURING AN<br>UNSATURATED POLYESTER<br>RESIN PANEL                        |
| FOREIGN TITLE                 | [54A]: | Fuhowa Poriesuteru<br>Jushi Ban no Sei Ho   |

#### Specification

#### 1. Title of the invention

Method for manufacturing an unsaturated polyester resin panel

#### 2. Patent Claims

- 1. A method for manufacturing an unsaturated polyester resin panel characterized by the facts that a laminate is prepared by laminating an epoxy resin-impregnated prepreg(s) on at least one plane of an unsaturated polyester resin layer prior to the commencement of the curing thereof by means at least either of light irradiation & heating, that the resin layer within said laminate is irradiated with light via said epoxy resin-impregnated prepreg, and that said laminate is then thermally molded.
- 2. A method for manufacturing an unsaturated polyester resin panel mentioned in Claim 1 wherein the aforementioned laminate is thermally molded after the lamination additionally of a thin film-formable material(s) above the aforementioned laminated epoxy resin-impregnated prepreg(s).
- A method for manufacturing an unsaturated polyester resin panel mentioned in Claim 2 wherein the aforementioned thin film-formable material(s) is a copper foil(s).

## 3. Detailed explanation of the invention

The present invention concerns a method for manufacturing an unsaturated polyester resin panel.

An unsaturated polyester resin panel has, in the prior art, been manufactured by preparing a sheet-shaped moldable material provided by viscosifying, with magnesium oxide, etc., a mixture of an unsaturated polyester resin, a glass fiber, an inorganic filler, etc. and by molding said material in a pressed & heated state. It is difficult, however, to prepare a flat panel bearing an excellent thickness precision from such a moldable material due to a profuse resin flow volume at the time of molding. The adhesion contiguities of unsaturated

polyester resins with thin film-formable materials such as a copper foil, film, aluminum foil, etc., furthermore, are inferior, and it has therefore been impossible to laminate thin filmformable materials such as copper foils, etc. at the time of molding. The method shown in Figure 1 has been proposed for the purpose of eradicating such shortcomings. In other words, according to this method, a sheet-shaped moldable material is prepared by irradiating & curing frontal & rear planes of an unsaturated polyester resin layer (1) inclusive of optical & thermal polymerization starters (unsaturated polyester resin A stage) with ultraviolet rays (2) (unsaturated polyester resin B stage) and by laminating unsaturated polyester resinimpregnated prepregs (3) on frontal & rear planes of said cured product, whereas an unsaturated polyester resin panel (4) is manufactured as a result of the C stage conversion of the unsaturated polyester resin based on a molding operation in a pressed & heated state. According to this method, the unsaturated polyester resin layer within the sheet-shaped moldable material has already been cured, and since the resin fluidity at the time of molding is minimal, it becomes possible to manufacture a flat panel bearing a rather favorable thickness precision. Since unsaturated polyester resin-impregnated prepregs exist on both frontal & rear planes of the resin layer, furthermore, even a thin film-formable material such as a copper foil can be laminated at the time of molding. Since both frontal & rear planes of the unsaturated polyester resin layer are directly irradiated with ultraviolet rays according to this method, however, the resins on the frontal & rear plane of the unsaturated polyester resin layer cannot be converted, in the course of irradiation, into the B stage and remain at the A stage due to the effects of oxygen in the air, and accordingly, the resin in the interior layer alone becomes converted into the B stage. On an occasion where the frontal & rear planes of the unsaturated polyester resin layer are laminated with prepregs and then pressed & heated, therefore, the resins (A stage) flow on the frontal & rear plane portions of the unsaturated polyester resin layer, and accordingly, the concomitantly achieved thickness precision may be rather favorable but not fully satisfactory.

The objective of the present invention is therefore to provide a method capable of manufacturing an unsaturated polyester resin panel bearing a further advanced thickness precision.

In summary, the present invention attempts, as Figure 2 indicates, to prepare a laminate (7) by laminating an epoxy resin-impregnated prepreg(s) (6) on at least one plane of an unsaturated polyester resin layer (5) prior to the commencement of the curing thereof by means at least either of light irradiation & heating and to manufacture an unsaturated polyester resin panel (9) bearing an excellent thickness precision by irradiating the resin layer (5) within said laminate (7) with a light (8) via said prepreg(s) (6) for inducing the B stage conversion of said resin and by then thermally molding said laminate (7) for inducing the C stage conversion of said resin.

In other words, as far as the present invention is concerned, the unsaturated polyester resin layer (5) is irradiated with the light (8) via the epoxy resin-impregnated prepreg(s) (6) rather than directly, and therefore, it is not affected by oxygen in the air at the time of irradiation. For this reason, resins not only in the interior of the unsaturated polyester resin layer (5) but also on the outer plane(s) thereof become homogeneously converted into the B stage. As a result, no resin fluidization occurs at the time of thermal molding, and it therefore becomes possible to obtain an unsaturated polyester resin panel (9) bearing an extremely advanced thickness precision. Since the epoxy resin-impregnated prepreg (6) bears, in comparison with an unsaturated polyester resin-impregnated prepreg, an extremely high adhesion contiguity with a thin film-formable material (e.g., copper foil, etc.), an extremely firm & contiguous adhesion state can be achieved on an occasion for laminating a thin film-formable material.

Next, the present invention will be explained in detail.

The present invention uses an unsaturated polyester resin layer wherein the curing thereof becomes initialized by means of light irradiation and/or heating. Such a resin layer may, for example, be prepared by mixing & kneading a resin layer-formable composition bearing the prescription shown below by using a kneading machine (e.g., kneader, roll, etc.) and by processing the obtained mixture into a sheet bearing, preferably, a thickness of  $0.5 \sim 5$  mm by using an extruding machine, calender roll, press, etc.

## (Composition)

Unsaturated polyester resin: 100 parts by weight;

Cross-linking agent: 5 ~ 50 parts by weight;

Optical polymerization starter:  $0 \sim 2$  parts by weight;

Thermal polymerization starter: 1 ~ 10 parts by weight;

Thermal polymerization inhibitor: 0.01 ~ 1 part by weight;

Filler:  $0 \sim 500$  parts by weight;

Reinforcement: 0 ~ 500 parts by weight.

Usable unsaturated polyester resins may, for example, be instantiated by a product obtained by thermally polymerizing, with a glycol (e.g., ethylene glycol, polyethylene glycol, propylene glycol, polypropylene glycol, butanediol, neopentyl glycol, hydrogenated bisphenol A, etc.), an  $\alpha\beta$ -unsaturated dibasic acid(s) (e.g., maleic anhydride, fumaric acid, etc.) or, if necessary, a component obtained partially substituting the same with a saturated dibasic acid (e.g., phthalic anhydride, isophthalic acid, terephthalic acid, tetrachlorophthalic anhydride, HET acid, succinic acid, adipic acid, etc.) at a glycol-to-acid component molar ratio of nearly 1 : 1. Usable cross-linking agents are instantiated by vinyl-p-phenyl benzoate, allylurea, phenylmaleimide, maleimide, triallyl cyanurate, diallyl phthalate prepolymer, styrene, divinylbenzene, vinyltoluene, etc., whereas usable acrylic compound

/3

cross-linking agents are instantiated by acrylamide, methyl methacrylate, butyl methacrylate, ethylene glycol diacrylate, polyethylene glycol diacrylate, ethylene glycol dimethacrylate, polyethylene glycol dimethacrylate, trimethylolpropane dimethacrylate, epoxy acrylate, etc. Usable optical polymerization starters are instantiated by benzoin, benzoin methyl ether, benzoin ethyl ether, benzoin isoputyl ether, benzoin isoputyl ether,

benzyldiphenyl disulfide. diacetylbenzonhenone. 3-methylbenzophenone. 2.4dimethylbenzophenone, 4-acetylbenzophenone, 2-chlorobenzophenone, 2,4'chlorobenzophenone, anthraquinone, chloroanthraquinone, methylanthraquinone, etc. Usable thermal polymerization starters are instantiated by benzoyl peroxide, tert-butyl perbenzoate, dicumyl peroxide, methyl ethyl ketone peroxide, di-tert-butyl peroxide, cyclohexanone peroxide, 2,5-dimethyl-2,5-di(tert-butylperoxy)hexane, etc. Usable fillers are instantiated by calcium carbonate, silica powder, hydrated alumina, clay, talc, kaolin, diatomaceous earth, glass powder, polyethylene, polystyrene, polymethyl methacrylate, etc., whereas usable reinforcements are instantiated by a glass fiber, asbestos, vinylon fiber, nylon fiber, glass cloth, glass mat, asbestos paper, synthetic fiber cloth, synthetic fiber mat, paper, cotton cloth, etc.

Moreover, an unsaturated polyester resin layer can also be prepared by dissolving a resin layer-formable composition into acetone, methyl ethyl ketone, toluene, dimethylformamide, etc., by impregnating a substrate (e.g., glass cloth, paper, etc.) with the obtained solution, and by drying the same. It is necessary to initialize the curing of such an unsaturated polyester resin layer by means of light irradiation and/or heating. For this reason, the optical polymerization starter & thermal polymerization starter are mixed with the resin layer-formable composition, whereas the polymerization of said unsaturated polyester resin is initialized by means of light irradiation or heating, as a result of which the resin layer becomes cured. The polymerizations of some unsaturated polyester resins {e.g., resin using itaconic acid and/or itaconic anhydride as a partial unsaturated dibasic acid component(s), resin obtained by partially esterifying polyvinyl alcohol with cinnamic acid, etc.}, however, become initialized by means of light irradiation even in the absence of optical polymerization starters, and in cases where these resins are used, there is no need to mix optical polymerization starters.

Moreover, in a case where a mixture of two or more types of unsaturated polyester resins bearing mutually different iodine values are used as said unsaturated polyester resin, it becomes possible, on an occasion for curing an unsaturated polyester resin layer by means of light irradiation, to further mitigate the B stage conversion heterogeneity of the resin. For this reason, the thickness precision of the obtained unsaturated polyester resin panel becomes further upped. The goal of mitigating the B stage conversion heterogeneity can also be realized by using an acrylic compound & an ethylenic unsaturated compound jointly as cross-linking agents. This goal can also be realized by using two or more types of optical polymerization starters.

The epoxy resin-impregnated prepreg to be laminated on one or both planes of the unsaturated polyester resin layer may, for example, be prepared by dissolving, into a solvent, a prepreg-formable composition comprising of an epoxy resin or terminal-acryl-modified epoxy resin & a curing agent (ordinary curing agents of the amine or carboxylic acid type are used in the case of epoxy resins, or radical polymerization starters are used as curing agents in the case of terminal-acryl-modified epoxy resins) as well as, if necessary, a filler (e.g., calcium carbonate, hydrated alumina, clay, antimony trioxide, titanium oxide, etc.), by impregnating a substrate with the obtained resin varnish, and by then drying the same. A laminate is then prepared by laminating the obtained prepreg(s) on a resin layer. In the above, usable solvents may, for example, be instantiated by acetone, methyl ethyl ketone, dimethylformamide, etc., whereas usable substrates are instantiated by a glass cloth, glass mat, asbestos paper, synthetic fiber cloth, synthetic fiber mat, paper, cotton cloth, etc.

In a case where the unsaturated polyester resin layer within this laminate is irradiated with light, above all ultraviolet rays, via said prepreg(s), said ultraviolet rays, etc. are irradiated for 10 sec. to 10 min. by using an ultraviolet lamp (e.g., low-pressure mercury lamp, high-pressure mercury lamp, etc.). As a result, the resin within the unsaturated

/4

polyester resin layer becomes homogeneously converted into the B stage. In other words, the resins not only in the interior of the resin layer but also on the outer plane(s) thereof become homogeneously converted into the B stage.

The laminate is thermally molded according to ordinary procedures. In this case, it is also possible to laminate a thin film-formable material (e.g., copper foil, etc.) at the time of molding.

The unsaturated polyester resin panel thus obtained bears an extremely high dimensional precision.

Next, application examples will be explained together with comparative examples.

# Application Example 1

An unsaturated polyester resin (A) bearing an acid value of 22, an iodine value of 68, & a softening point of 78°C was obtained by reacting 1 mole of isophthalic acid, 2.1 mole of propylene glycol, & 1 mole of fumaric acid within a nitrogen gas stream at 160 ~ 210°C.

100 parts by weight (hereafter abbreviated as "parts") of said unsaturated polyester resin (A), 30 parts of a diallyl phthalate prepolymer, 3 parts of dicumyl peroxide, 0.2 part of benzoin, 0.03 part of hydroquinone, 100 parts of calcium carbonate, 150 parts of hydrated alumina, & 100 parts of a glass fiber were kneaded within a compressive kneader heated at 60°C over a 15-min. period, as a result of which an unsaturated polyester resin moldable material was obtained.

A prepreg, on the other hand, was obtained by impregnating a glass cloth with a varnish comprising of 100 parts of an epoxy resin (Epikote 1001, manufactured by Shell Chemical Co.), 4 parts of a curing agent (dicyanodiamide), & 300 parts of acetone and by then drying the same at 100°C.

Next, the above-mentioned unsaturated polyester resin moldable material was sandwiched in-between a pair of said prepregs, and after the obtained laminate had been molded by using spacers bearing a gap length of 1.2 mm under conditions of 90°C, 100 kg/cm², & 1 min., a sheet-shaped laminate with a thickness of 1.2 mm was obtained. Next, said laminate was irradiated with ultraviolet rays emitted from an 80 W mercury lamp over a

60-sec. period. Next, a copper foil was laminated above said sheet-shaped laminate, and after the obtained structure had then been molded in a heated & pressed state at 170°C & 80 kg[/cm²?] over a 30-min. period, a single-sided copper-pasted laminate sheet was obtained.

#### Comparative Example 1

A single-sided copper-pasted laminate sheet was obtained according to procedures similar to those in Application Example 1 except that the ultraviolet irradiation of Application Example 1 was dispensed with.

#### Comparative Example 2

A single-sided copper-pasted laminate sheet was obtained according to procedures similar to those in Application Example 1 except that the epoxy resin-impregnated prepreg used in Application Example 1 was substituted with an unsaturated polyester resin-impregnated prepreg obtained by impregnating a glass cloth with 100 parts of the above-mentioned unsaturated polyester resin (A), 30 parts of a diallyl phthalate prepolymer, 3 parts of dicumyl peroxide, & 300 parts of acetone.

#### Application Example 2

A prepreg was obtained by immersing a glass cloth within a varnish comprising of 100 parts of a terminal-acryl-modified epoxy resin (Lipoxy VR60, manufactured by Showa Polymer Co.), 20 parts of a diallyl phthalate prepolymer, 4 parts of tert-butyl perbenzoate, & 200 parts of methyl ethyl ketone and by then drying said cloth. The unsaturated polyester resin moldable material prepared in Application Example 1 was sandwiched in-between a pair of said prepregs, and the obtained structure was then molded under conditions of 90°C, 100 kg/cm², & 1-min. by using 1.2 mm spacers, as a result of which a sheet-shaped laminate with a thickness of 1.2 mm was obtained. Next, said laminate was irradiated with ultraviolet rays emitted from an 80 W mercury lamp over a 45-sec. period, and after a copper foil had

been laminated above the same, the obtained structure was molded in a heated & pressed state under molding conditions of 170°C, 100 kg/cm<sup>2</sup>, & 10 min., as a result of which a single-sided copper-pasted laminate sheet was obtained.

#### Application Example 3

1 mole of dimethyl terephthalate, 1 mole of propylene glycol, 1.1 mole of ethylene glycol, & 1.1 parts of zinc acetate were reacted with one another within a nitrogen gas stream at 160°C ~ 190°C, and after 1 mole of maleic anhydride had been added at a stage where 95% of the theoretical equivalent of methanol had become distilled, the contents were further reacted at 160°C ~ 210°C, as a result of an unsaturated polyester resin (B) bearing an acid value of 24, an iodine value of 73, & a softening point of 84°C was obtained.

A varnish was prepared by mixing 100 parts of this unsaturated polyester resin (B) with 30 parts of a dillyl phthalate prepolymer, 0.5 part of benzophenone, 0.05 part of hydroquinone, 3 parts of tert-butyl perbenzoate, & 200 parts of acetone. Next, a glass cloth was immersed within this varnish and then dried, as a result of which an unsaturated polyester resin-impregnated prepreg was obtained.

/<u>5</u>

An epoxy resin-impregnated prepreg, on the other hand, was obtained by immersing a glass cloth within a varnish comprising of 100 parts of an epoxy resin (DER 511, manufactured by Dow Co.), 3.5 parts of curing agent (dicyanodiamide), & 150 parts of acetone and by then drying the same at 100°C.

Next, eight polyester resin-impregnated prepregs were sandwiched in-between a pair of said epoxy resin-impregnated prepregs, and after the obtained structure had been molded under conditions of 50°C, 40 kg/cm², & 1 min., a sheet-shaped laminate with a thickness of 1.5 mm was obtained. After said laminate had been irradiated with an 80 W mercury lamp over a 30-sec, period, copper foils was laminated on the same, and after the obtained

structure had been molded in a heated & pressed state under molding conditions of 170°C, 80 kg/cm<sup>2</sup>, & 30 min., a double-sided copper-pasted laminate sheet was obtained.

#### Comparative Example 3

A double-sided copper-pasted laminate sheet was obtained according to procedures similar to those in Application Example 3 except that the ultraviolet irradiation of Application Example 3 was dispensed with.

## Application Example 4

0.5 mole of isophthalic acid, 0.5 mole of phthalic anhydride, & 2.1 mole of propylene glycol were reacted with one another until the achievement of an acid value of 6, and after 1 mole of itaconic acid had been further added, the reaction was continued, as a result of which an unsaturated polyester resin (C) bearing an acid value of 25, an iodine value of 65, & a softening point of 69°C was obtained.

A varnish was prepared by mixing 100 parts of this unsaturated polyester resin (C) with 30 parts of a diallyl phthalate prepolymer, 4 parts of tert-butyl perbenzoate, 0.02 part of benzoquinone, & 100 parts of toluene. This varnish was sprayed onto glass fiber chopped strands and then dried at 120°C, as a result of which a prepreg mat was obtained.

An epoxy resin-impregnated prepreg, on the other hand, was obtained by immersing a glass cloth within a varnish comprising of 100 parts of an epoxy resin (Epikote 1045, manufactured by Shell Co.), 4 parts of a curing agent (dicyanodiamide), & 100 parts of toluene and by then drying the same at 120°C.

Next, the aforementioned prepreg mat was sandwiched in-between a pair of said epoxy resin-impregnated prepregs, and the obtained structure was molded by using 1.5 mm spacers under conditions of 80°C, 100 kg/cm², & 1 min., as a result of which a sheet-shaped laminate with a thickness of 1.5 mm was obtained. Next, said laminate was irradiated with an 80 W mercury lamp over a 60-sec. period, and after copper foils had been laminated on

the same, the obtained structure was molded in a heated & pressed state under conditions of 170°C, 60 kg/cm<sup>2</sup>, & 30 min., as a result of which a double-sided copper-pasted laminate sheet was obtained.

#### Reference Example

100 parts of the unsaturated polyester resin (B) of Application Example 3, 10 parts of ethylene glycol dimethacrylate, 4 parts of dicumyl peroxide, 0.5 part of benzoin isopropyl ether, 0.02 part of benzoquinone, 200 parts of calcium carbonate, & 70 parts of a glass fiber were kneaded within a compressive kneader being heated at 60°C over a 10-min. period, as a result of which an unsaturated polyester resin moldable material was obtained. After a sheet-shaped object with a thickness of 1.5 mm had been molded from this material by using 1.5 mm spacers under conditions of 90°C & 100 kg/cm², it was irradiated with ultraviolet rays emitted from an 80 W mercury lamp over a 60-sec. period.

A varnish comprising of 100 parts of an epoxy resin (Epichlone 1051, manufactured by Dainihon ink Co.), 4 parts of a curing agent (BF<sub>3</sub> 400), & 200 parts of acetone, on the other hand, was coated on a copper foil and then dried at 100°C, as a result of which an adhesive-pasted copper foil was obtained.

Next, said adhesive-pasted copper foil was laminated on an unsaturated polyester resin panel, and the obtained structure was molded in a heated & pressed state under conditions of 170°C, 50 kg/cm<sup>2</sup>, & 30 min., as a result of which a double-sided copper-pasted laminate sheet was obtained.

The characteristics of the respective laminate panels obtained in the foregoing application examples, comparative examples, & reference example were measured according to the test procedures of JIS C 6484. The results are shown in Table I.

#### [END OF PAGE]

Table I (Part 1)

| Solder heat resistance (260°C)   |                        | Application Example 1 At least 45 sec. | Application Example 2 At least 45 sec. | Application Example 3 At least 45 sec. | Application Example 4 At least 45 sec. |
|----------------------------------|------------------------|--|--|--|--|
| Peeling strength (kg/cm²)        | Normal state           | 2.1                                    | 1.8                                    | 1.9                                    | 1.8                                    |
|                                  | After solder treatment | 2.1                                    | 1.8                                    | 1.9                                    | 1.8                                    |
| Insulation resistance $(\Omega)$ | Normal state           | 8 × 10 <sup>13</sup>                   | 2 × 10 <sup>14</sup>                   | 3 × 10 <sup>14</sup>                   | 7 × 10 <sup>13</sup>                   |
|                                  | After treatment        | $7 \times 10^{12}$                     | 5 × 10 <sup>13</sup>                   | $6 \times 10^{13}$                     | 9 × 10 <sup>12</sup>                   |
| Laminate sheet thickness (mm)    | Before molding         | 1.2                                    | 1.2                                    | 1.5                                    | 1.5                                    |
|                                  | After molding          | 1.2                                    | 1.2                                    | 1.5                                    | 1.5                                    |

Table I (Part 2)

| Solder heat resistance (260°C)   |                        | Comparative Example 1 15 sec. | Comparative Example 2 35 sec. | Comparative Example 3 20 sec. | Reference<br>example<br>At least 45<br>sec. |
|----------------------------------|------------------------|-------------------------------|-------------------------------|-------------------------------|---|
| Peeling strength (kg/cm²)        | Normal state           | 1.2                           | 1.5                           | 1.2                           | 2.2   |
|                                  | After solder treatment | Peeling due to swelling       | 1.3                           | Peeling due to swelling       | 2.1   |
| Insulation resistance $(\Omega)$ | Normal state           | 5 × 10 <sup>13</sup>          | 8 × 10 <sup>13</sup>          | $3\times10^{14}$              | 6 × 10 <sup>13</sup>                        |
|                                  | After treatment        | 3 × 10 <sup>10</sup>          | 5 × 10 <sup>10</sup>          | $9\times10^{10}$              | 2 × 10 <sup>13</sup>                        |
| Laminate sheet<br>thickness (mm) | Before<br>molding      | 1.2                           | 1.2                           | 1.5                           | 1.5   |
|                                  | After<br>molding       | 0.4                           | 1.1                           | 1.0                           | 1.5   |

[Note: "After solder treatment" means after a 30-sec. immersion within a 260°C solder bath]

As the table clearly indicates, the dimensional precisions of the respective samples of the application examples were extremely high, and furthermore, the adhesion contiguities of copper foils are excellent. Next, extents to which irregularities of progresses of B stage conversions of resins on light irradiation occasions are mitigated in a case where two or more types of unsaturated polyester resins bearing mutually different iodine values are used (Application Examples 5 & 8), a case where an acrylic compound & an ethylenic unsaturated compound are used together as cross-linking agents (Application Examples 6 & 8), and a case where two or more types of optical polymerization starters are used (Application Examples 7 & 8) will be explained together with comparative examples.

## Application Example 5

1.5 mole of isophthalic acid, 2.1 mole of propylene glycol, & 0.5 mole of fumaric acid were reacted with one another within a nitrogen gas stream at  $160 \sim 210^{\circ}$ C, as a result of which an unsaturated polyester resin (D) bearing an acid value of 27, an iodine value of 32, & a softening point of 81°C was obtained. Moreover, 0.7 mole of isophthalic acid, 2.1 mole of propylene glycol, & 1.3 mole of fumaric acid were reacted with one another within a nitrogen gas stream at  $160 \sim 210^{\circ}$ C, as a result of which an unsaturated polyester resin (E) bearing an acid value of 23, an iodine value of 98, & a softening point of 71°C was obtained.

Next, 25 parts of the unsaturated polyester resin (D), 25 parts of the unsaturated polyester resin (E), 50 parts of the unsaturated polyester resin (A) of Application Example 1, 30 parts of a diallyl phthalate prepolymer, 3 parts of dicumyl peroxide, 0.4 part of benzoin isopropyl ether, 0.02 part of benzoquinone, & 200 parts of calcium carbonate were charged into a 60°C compressive kneader and then kneaded over a 20-min. period, as a result of which a moldable material was obtained.

Next, said material was molded by using 1.5 mm spacers under conditions of 100°C, 100 kg/cm<sup>2</sup>, & 1 min. and then cut by using a cutter, as a result of which ten square pieces with a side dimension of 2 cm were obtained. Next, the respective pieces were irradiated with an 80 W mercury lamp for 60 sec. each, as a result of which B-stage products were obtained.

#### Application Example 6

A moldable material comprising of 100 parts of the unsaturated polyester resin (A) of Application Example 1, 5 parts of trimethylolpropane triacrylate, 25 parts of a diallyl phthalate prepolymer, 3 parts of dicumyl peroxide, 0.4 part of benzoin isopropyl ether, 0.02 part of benzoquinone, & 200 parts of calcium carbonate was prepared, and ten B-stage products were obtained from the same according to procedures otherwise similar to those in Application Example 5.

# Application Example 7

A moldable material comprising of 100 parts of the unsaturated polyester resin (A) of Application Example 1, 30 parts of a diallyl phthalate prepolymer, 3 parts of dicumyl peroxide, 0.2 part of benzoin isopropyl ether, 0.1 part of benzophenone, 0.1 part of anthraquinone, 0.02 part of benzoquinone, & 200 parts of calcium carbonate was prepared, and ten B-stage products were obtained from the same according to procedures otherwise similar to those in Application Example 5.

#### Application Example 8

A moldable material comprising of 50 parts of the unsaturated polyester resin (A) of Application Example 1, 25 parts of the unsaturated polyester resin (D) of Application Example 5, 25 parts of the unsaturated polyester resin (E) of Application Example 5, 5 parts of ethylene glycol dimethacrylate, 25 parts of a diallyl phthalate prepolymer, 3 parts of dicumyl peroxide, 0.2 part of benzoni isopropyl ether, 0.2 part of benzophenone, 0.02 part of benzoquinone, & 200 parts of calcium carbonate was prepared, and ten B-stage products

/7

were obtained from the same according to procedures otherwise similar to those in Application Example 5.

#### Comparative Example 4

A moldable material comprising of 100 parts of the unsaturated polyester resin (A) of Application Example 1, 30 parts of a diallyl phthalate prepolymer, 3 parts of dicumyl peroxide, 0.4 part of benzoin isopropyl ether, 0.02 part of benzoquinone, & 200 parts of calcium carbonate was prepared, and ten B-stage products were obtained from the same according to procedures otherwise similar to those in Application Example 5.

Ten B-stage products each obtained in Application Examples 5 ~ 8 & Comparative Example 4 were immersed within a 60°C methyl ethyl ketone over a 2-hour period, and their extraction ratios were calculated. The results are shown in Table II.

Table II

|                      |               | AE 5 | AE 6 | AE 7 | AE 8 | CE 4 |
|----------------------|---------------|------|------|------|------|------|
| Extraction ratio (%) | Average value | 6.2  | 5.7  | 6.5  | 6.9  | 6.3  |
|                      | Variance      | 1.2  | 0.9  | 1.3  | 0.6  | 3.9  |

[(AE): Application Example; (CE): Comparative Example]

As the results of the table clearly indicate, the B-stage conversion irregularities of the respective samples of the application examples are extremely miniscule.

#### 4. Brief explanation of the figures

Figure 1 is a demonstrational diagram pertaining to the manufacturing scheme of an embodiment of the prior art, whereas Figure 2 is a demonstrational diagram pertaining to the manufacturing scheme of an embodiment of the present invention.

(5): Unsaturated polyester resin layer; (6): Epoxy resin-impregnated prepreg; (7): Laminate; (8): Light; (9): Unsaturated polyester resin panel.

Patent Applicant: Matsushita Denko Co., Ltd.

Agents: Toshimaru Takemoto, patent attorney, and 2 others

Figure 1

Figure 2

